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Moisture sorption isotherms and thermodynamic properties of whole black peppercorns (*Piper nigrum* L.)

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Abstract

Adsorption and desorption isotherms for whole black peppercorns (*Piper nigrum* L.) were developed at 22, 30 and 37°C using the standard static gravimetric method. The sorption isotherms exhibited a type III behavior according to Brunauer-Emmett-Teller (BET) classifications. The equilibrium moisture content (EMC) decreased with increasing temperature at a particular water activity (a_w). Hysteresis existed over the entire a_w range at 30 and 37°C. At 22°C, an intersection of the curves was found at a_w closer to 0.75. The goodness of fit of the models was evaluated using several statistical indices and residual plots. The Guggenheim-Anderson-de Boer (GAB) and Peleg models were determined to best describe the experimental sorption data. The monolayer moisture content (M_0) were 4.78, 3.56 and 3.49% at 22, 30 and 37°C for adsorption. The maximum isosteric heat of sorption was 28.1 and 73.3 kJ/mol for adsorption and desorption, respectively. The net isosteric heat of sorption and sorption entropy increased with increase in EMC; both curves dropped off exponentially after M_0. The Gibbs free energy change for adsorption ($-\Delta G$) ranged from 100.6-9370.6 J/mol depending on the temperature and EMC (1-40%). The study has provided useful information for industrial drying, processing and storage of whole black peppercorns.

Keywords: Black peppercorns, Moisture isotherms, Adsorption, Desorption, Isosteric heat

1. Introduction

Black pepper (*Piper nigrum* L.), well known as "the king of spices", fetches the highest return as estimated from the volume of international trade. It is widely used around the world due to its pungent property and serves in many other purposes such as medicinal, preservation and insecticide (Srinivasan, 2007). Similar to many other spices, they are mainly cultivated in tropical/semi-tropical countries and dried under the sun in open air. Apart from the climatic conditions, lack of Good Agricultural Practices (GAP) and Good Manufacturing Practices (GMP) are of great concern in developing countries where peppers are grown. Similar to many other dry foods, black peppers are susceptible for microbial spoilage and toxin production if their water activity (a_w) exceeds the safe limits and if storage temperature is suitable for microbial growth. They are often contaminated with several fungal species and more specifically with *Aspergillus* species which produce toxic secondary metabolites like aflatoxins and ochratoxin A (Yogendrarajah et al., 2014).

The quality of most foods preserved by drying depends to a great extent upon their physical, chemical and microbiological stability. This stability is partly a consequence of the relationship between the equilibrium moisture content (EMC) of the food material and its a_w, at a given temperature. This relationship is described by moisture sorption isotherms. Moisture sorption isotherms are unique for individual food matrices and they are essential for modelling drying processes, design and optimization of drying equipment, predicting shelf-life stability, calculating moisture changes which may occur during storage and in selecting appropriate packaging material (Gal, 1987). Since, the quality of spices is markedly dependent on colour and flavour retention, it is essential to dry them to critical a_w values that preserve their quality by preventing oxidation of essential oils and enzymatic or microbial spoilage (Marcos et al., 1997). The determination of such critical values allows the establishment of reasonable drying and storage limits for black peppers.

Numerous empirical and semi-empirical models are available that can be used to predict the moisture sorption properties of foods; kinetic models based on a mono-layer (modified BET (Brunauer-Emmett-Teller) model), kinetic models based on a multi-layer and condensed film (Guggenheim-Anderson and de Boer (GAB) model), semi-empirical (Ferro-Fontan, Henderson and Halsey models) and empirical models (Smith and Oswin models) (Al-Muhtaseb et al., 2010). The best known two parameter homogenous model is the BET model but its applicability is limited to a_w range 0.5 to 0.45 (Al-Muhtaseb et al., 2002). The three parameter GAB model has been extensively used up to a_w of 0.9; above 0.9 it usually predicts less water content than that measured experimentally. Both models assume homogeneous sorption with water forming a mono-molecular layer initially, while the additional water forms a multilayer (Yanniotis and Blahovec, 2009). Monolayer moisture content (M_0) is of significant importance for the stability of food with regard

to lipid oxidation, enzyme activity, non-enzymatic browning and structural characteristics. According to Lomauro et al. (1985) the GAB equation gave the best fit for more than 50% of the fruits, meats and vegetables than the two parameter models after evaluating 163 food materials including fruits, vegetables, spices and starchy foods. A fourth parameter to the GAB equation was introduced by Viollaz and Rovedo (1999) in order to correlate the sorption data for a_w higher than 0.9. Moreover, Peleg (1993) proposed a four parameter model that can be used for both sigmoid and non-sigmoid isotherms, and it fitted as well as, or better than the GAB model. The Langmuir model is one of the well-known model and it has been extensively used in surface chemistry (Bretag et al., 2009).

Nonetheless, it has been already noted that no sorption isotherm model could fit data over the entire range of relative humidity (RH) because water is associated with the food matrix by different mechanisms in different activity regions. A detailed research of the literature showed that moisture sorption isotherms of foods can be described by more than one sorption model (Lomauro et al., 1985).

Although moisture sorption isotherm models have been developed for several food matrices, to date none have been developed for whole black peppercorns. Hence, the main objectives of the present study are to a) determine the adsorption and desorption isotherms of black peppercorns at temperatures 22, 30 and 37°C, b) evaluate the ability of several commonly used sorption models to describe the experimental data and c) determine the thermodynamics of the sorption phenomenon.

2. Materials and methods

2.1. Materials

Whole black peppercorns (*Piper nigrum* L.) used in this study were of Sri Lankan origin purchased from local market in Jaffna, Sri Lanka. The peppercorns had an initial moisture content of 12.5±0.7 g/100g dry matter and a_w of 0.60±0.06. The saturated salts used were of analytical grade.

2.2. Experimental procedure

Adsorption and desorption isotherms of the black pepper whole corns were determined at 22, 30 and 37°C, over a a_w range of 0.13-0.97 using the static gravimetric method. The equilibrium moisture contents (EMCs) were determined at various equilibrium relative humidity's (ERHs, 13-97%) for both desorption and adsorption isotherms. For the adsorption isotherms the peppercorns were first dried in sealed jars over pure sulphuric acid (95%) until the weight loss was negligible. This took approximately one week and resulted in peppercorns with a a_w of 0.137±0.002. For the desorption isotherms, the peppers were first placed over water in sealed jars until no appreciable weight gain was noticed. This took *ca*. four weeks. Saturated salt solutions were prepared to achieve different ERHs; potassium acetate (23.1%), potassium carbonate (43.2%), magnesium nitrate (54.4%), sodium bromide (57.7%), potassium iodide (69.9%), sodium chloride (75.5%), ammonium sulfate (81.3%), potassium chloride (85.1%), potassium nitrate (94.6%) and potassium sulfate (97.6%). The ERHs given above are those achieved at 20°C. The saturated salt solutions were placed in sealable plastic containers. Five grams of whole black peppercorns were placed in perforated aluminum cups and placed inside the containers with the saturated salt solutions. The cups were kept from coming into contact with the saturated salt solutions by means of a platform fashioned from chicken wire mesh. Four replicates were prepared for each condition (ERH and temperature) evaluated. Toluene (5 mL in an open container) was also placed inside each container to prevent any fungal growth; regularly checked and refilled when necessary. The containers were then tightly closed and placed in the incubators at different temperatures (22, 30 and 37°C) for equilibration. The initial weight of the peppercorn samples together with the aluminum cups was recorded. The weight of the samples were recorded every week to check if the sample had equilibrated with the respective ERH. When there were no significant differences in weight they were removed from the incubator for measurement of the a_w and moisture content. The a_w values were measured using a water activity meter (Novasina LabMaster, Lachen SZ, Switzerland). The corresponding EMCs were determined by oven drying method (AOAC, 1980).

2.3. Modelling of sorption isotherms

The equations shown in Table 1 (except 3 and 4) were fitted to the experimental data. These sorption models are widely used for describing the sorption isotherms of food materials. The goodness of fit of the model was evaluated by using the mean relative percentage deviation modulus (*P*) (Eq. 14).

$$P\ (\%) = \frac{100}{n}\sum_{i=1}^{n}\frac{|\mathrm{EMC}_{exp,i} - \mathrm{EMC}_{pred,i}|}{\mathrm{EMC}_{exp,i}} \quad (14)$$

According to Lamauro et al. (1985), if the *P* value is less than 10% the model is considered to be acceptable.

Moreover, the accuracy of fit of the models was evaluated by calculating the root mean square error (RMSE %) between the experimental and predicted EMCs (Eq. 15).

$$\mathrm{RMSE} = \sqrt{\frac{1}{\mathrm{N}}\left[\sum_{i=1}^{N}(\mathrm{EMC}_{exp,i} - \mathrm{EMC}_{pred,i})^2\right]} \quad (15)$$

The suitability of the models were further evaluated by calculating the reduced chi square (χ^2) (Eq. 16).

$$\chi 2 = \frac{\sum_{i=1}^{N}\left(\mathrm{EMC}_{exp,i} - \mathrm{EMC}_{pred,i}\right)^2}{\mathrm{N-n}} \quad (16)$$

In Eq.'s. 14, 15 and 16, $\mathrm{EMC}_{exp,i}$ is the i^{th} value of the experimentally measured EMC, $\mathrm{EMC}_{pred,i}$ is the i^{th} predicted value of the EMC, N is the number of observations (data points) and n is the number of constants. A model was considered good when the R^2 is high and the RMSE, *P*(%) and reduced chi square values were low.

Moreover, standardized residuals (residual sums of squares, Eq. 17) were plotted as a function of the a_w values. A model is considered acceptable if the residual values are located in a horizontal band centered around zero, displaying no systematic tendencies towards a clear pattern. If the residual plot indicates clear pattern, the model is considered unacceptable or biased.

$$\mathrm{RSS} = \sum_{i=1}^{n}\left(\mathrm{EMC}_{exp,i} - \mathrm{EMC}_{pred.i}\right)^2 \quad (17)$$

2.4. Thermodynamic properties of sorption phenomena

The thermodynamic properties of the sorption phenomena were evaluated in terms of net isosteric heat of sorption, Gibbs free energy, sorption entropy and binding energy in the whole black peppercorn-water system.

2.4.1. Determination of net isosteric heat of sorption

The net isosteric heat of sorption or enthalpy of sorption (q_{st}) is defined as the difference between the total heat of sorption (Q_{st}) and the heat of vaporization of water. The net isosteric heat of sorption is given by:

$$q_{st} = Q_{st} - \Delta H vap \quad (18)$$

The net isosteric heat of adsorption and desorption for a given moisture content was calculated using the Clausius-Clapeyron equation (Eq. 19):

$$q_{st} = \frac{RT_1T_2}{T_2 - T_1} ln \frac{a_{w2}}{a_{w1}} \quad (19)$$

where R is universal gas constant (8.314 J/mol/K), a_{w2} and a_{w1} are the a_w values at absolute temperatures T_2 and T_1 (K), respectively. Δ*Hvap* is the heat of vapourisation (kJ/mol/K). qst was calculated from the slope developed by plotting *In* (a_w) versus 1/T for a specific moisture content. The slope equals $-q_{st}/R$ (Kiranoudis et al., 1993). The procedure was repeated for several EMCs to determine the relationship between the qst value and moisture content.

2.4.2. Determination of sorption entropy change

The sorption entropy change (ΔS) was determined using Eq. 20.

$$-In(a_w) = Q_{st}/(RT) - (\Delta S/R) \quad (20)$$

The EMC data from the GAB model was used to determine the sorption entropy at each moisture content. The sorption entropy for a given moisture level was calculated using the intercept (ΔS/R) of the curve of $In(a_w)$ versus 1/T.

2.4.3. Determination of Gibbs free energy change

The change in Gibbs' free energy (ΔG) was calculated using Eq. 21.

$$\Delta G = -RTln(a_w) \quad (21)$$

To determine the free energy change due to change in the moisture content in whole black peppercorns, a_w data were generated by the GAB models for the sorption isotherms. Free energy changes were then computed at several EMCs for each temperature evaluated in this study.

2.4.4. Determination of specific surface area of sorption

The specific surface area of sorption was determined using the following equation (Arslan and Toğrul, 2006):

$$S = M_0 \times N_A \times A_m / M_{wat} = 35.3/M_0 \quad (22)$$

where S is the solid surface area of sorption (m^2/g solids), M_0 the monolayer moisture content (%, dwb), N_A the Avogadro's number (6.02E+23 molecules/mol), A_m the area of a water molecule (1.06E-19 m^2/molecule) and M_{wat} is the molecular weight of the water (18 g/mol).

2.5. Statistical analysis

The statistical package SPSS (IBM®, Version 22) was used to estimate the parameters of the different models. Linear regression analysis was used to analyse the fit of the experimental data to the two parameter polynomial model whilst non-linear regression was used for the three and four parameter models. A one-way analysis of variance (ANOVA) was performed in order to identify the differences in EMCs between temperatures of both sorption isotherms.

3. Results and discussion

3.1. Desorption and adsorption moisture isotherms

The adsorption and desorption isotherms of whole black peppercorns developed at 22, 30 and 37°C are shown in Fig. 1. The EMCs of both the adsorption and desorption isotherms increased slowly between a_w values 0.2 and 0.75, followed by a steep rise at all the temperatures evaluated. Consequently, the sorption isotherms obtained in this investigation are type III (J shape) isotherms, which are characteristic of products holding small amounts of water at lower a_w values and higher amounts of water at high RH levels (Arslan and Toğrul, 2005). Similar behaviour has been reported previously in different food products i.e. sugars, apple, raisins, apricot, pineapple, beef (Al-Muhtaseb et al., 2002) and pistachio powder (Yazdani et al., 2006) and Madeira cake (Al-Muhtaseb et al., 2002). A type III isotherm appears when the binding energy for the first layer is lower than the binding energy between water molecules (Al-Muhtaseb et al., 2002). The desorption curves lie slightly above the adsorption curve showing some hysteresis. Hysteresis was observed over the entire a_w range at 30 and 37°C. However, at 22°C , an intersection of the curves was found at a_w *ca*. 0.75 (Fig. 2). Crossing over of the sorption isotherms at high a_w (>0.90) was also reported in the study of texturized soy protein which further states that the cross over a_w depends on the amount of sugar content (Cassini et al., 2006). Hysteresis has been related to the nature and state of the components in a food, reflecting their potential for structural and conformational rearrangements (Yan et al., 2008).

According to a one-way ANOVA, the EMCs of both adsorption and desorption isotherm at different temperatures was found to be insignificantly different (p>0.05). Similar trends have also been observed in other foods including tea (Arslan and Toğrul, 2006), buffalo skim milk (Sawhney et al., 2013) and crushed chillies (Arslan and Toğrul, 2005). It is widely accepted that an increase in temperature results in a decreased MC at a particular RH. Temperature affects the mobility of water molecules and the dynamic equilibrium between the vapour and adsorbed phases. At the lower a_w values the adsorption isotherms at 22 and 30°C and desorption isotherms at all three incubation temperatures were found to overlap (Fig. 2). The moisture sorption isotherms of grapes and apricot have also overlapped at several temperatures (Kaymak-Ertekin & Gedik, 2004). The difference in EMC at the three incubation temperatures investigated in this study, became more clear in both the adsorption and desorption isotherms at higher a_w values. According to Palipane & Driscoll (1992), increase in temperature activates water molecules to higher energy levels, allowing them to break away from their sorption sites, hence decreasing the EMC. As temperature varies, the excitation of molecules as well as the distance hence the attraction between molecules vary. This causes the amount of absorbed water to change with temperature at a given RH.

3.2. Fitting of sorption models to experimental data

As mentioned, eleven models were fitted to the experimental adsorption and desorption isotherm data. The best/moderately and poor fitting models are shown in Fig. 3a and 3b, respectively. The estimated parameters and the statistical indices used to evaluate the goodness of fit of each model are shown in Tables 2 and 3.

The GAB model estimated M_0's of 4.78, 3.56 and 3.49% (dwb) at 22, 30 and 37°C from the adsorption data. The desorption isotherms had higher M_0's of 4.67, 4.67 and 4.36% (dwb) at 22, 30 and 37°C , respectively. These results show that the M_0 decreases with increasing temperature. This could be due to the water molecules attaining the energy required to break away from their sorption sites at higher incubation temperatures, resulting in lower M_0's. The M_0 is a critical parameter as it represents the MC at which the rate of any associated reaction will be negligible due to the strong binding of water to the surface. An increase in a_w equivalent to an increase of M_0 by 0.1 units decreases the shelf life of a food product by a factor of 2-3 (Labuza, 1984). It is therefore an important quality parameter with regards to the designing optimal storage conditions for food products (Taitano et al., 2012). Therefore the M_0 values reported in this study represent the optimal MC for the storage of whole black peppercorns.

Moreover, as can be seen in Table 2, the estimated values of the GAB constant *C* (related to thermal effects) for adsorption were higher than those for desorption at all the temperatures evaluated. In agreement with the results of other products (Chirife et al., 1992), the estimated values for the constant *K* in the GAB model for both adsorption and desorption sorption isotherms were lower than unity. The physical meaning of *K* is related to the heat of adsorption of the multilayer. Moreover, the *C* values are much higher than *K* indicating that the heat of sorption of the first layer is greater than that of the multilayers.

As mentioned above, the goodness of fit of the models was assessed by means of coefficient of determination R^2, *P* (%), reduced chi squared value (χ^2), residual sums of square (RSS), residual average (R_{ave}), residual mean square error (RMSE) and the residual plots. Generally, a model with a *P* value of less than 10% is considered acceptable (Lomauro et al., 1985). According to the statistical indices, the model which fitted the experimental sorption data the best was the four parameter Peleg model which had R^2 values ≥0.98, the lowest *P* values (2.99-6.78%) and residual averages (-0.01-0.02) at all the temperatures experimented. According to the residual plots (Fig. 4a), this model also shows no bias. The second best fitting model was the GAB model (*P* values 5.47-11.68%), for both adsorption and desorption curves ($R^2 \geq$ 0.96). The residual plots show that in comparison to the Peleg model, the GAB model is slightly biased. The two parameter Oswin model and the modified Oswin model also had good fits to the experimental data with R^2 values ≥0.96 and *P* values ranging 4.89 to 15.3%. However, as observed for the GAB model, the Oswin model is slightly biased in comparison to the Peleg model, albeit less than the GAB model. The modified Mizrahi model also had good *P* values ranging from 4.28 to 9.38%, for both adsorption and desorption isotherms. However, in comparison to the excellent fit of the modified Mizrahi model on the desorption data, slightly lower R^2 values of 0.95 and 0.90 were obtained when the model was fitted to the adsorption isotherm data generated at 30 and 37°C , respectively. The double log polynomial (DLP) model was also determined to adequately fit the experimental sorption data with $R^2 \geq 0.93$ and *P* values ranging from 3.68 to 13.92%. The Caurie (R^2, 0.85-0.95; *P* (%), 17-27.68), Smith (R^2, 0.87-0.95; *P* (%), 11.74-19.84), modified

Henderson (R^2, 0.86-0.91; *P*(%) 10.96-15.82) and polynomial (R^2, 0.82-0.93; *P* (%) 18.25-29.81) models were found to inadequately fit the adsorption and desorption isotherms of whole black peppercorns (Fig. 3b and Table 3).

It can be seen in Fig. 4a and 4b that larger variability in the residuals can be observed at $a_w \geq 0.9$. There was a greater deviation between the values predicted by all the models and the experimental values. This has also been observed in modelling of the sorption isotherms of lemon peels (García-Pérez et al., 2008).

The validity of a sorption model cannot be proved just by its ability to fit the experimental data, a physico-chemical (mechanistic) basis is also needed (Chirife et al., 1992). Some of the parameters of the semi-empirical GAB model have theoretical basis compared to the entirely empirical Peleg model, which allow for the estimation of the M_0 as described previously. Despite that the Peleg model describes best the sorption isotherms of black peppercorns, the GAB model also performs adequately and can therefore be used to estimate the thermodynamic properties of the peppercorns. The GAB model has been reported as the best fitting model in several products i.e. potato, carrot, tomato, onion and green pepper (Kiranoudis et al., 1993), yellow dent corn (Samapundo et al., 2007), several fruits, vegetables and meat products (Lomauro et al., 1985) and lemon peel (García-Pérez et al., 2008). A modified GAB model best described the sorption data of maize flour (Oyelade et al., 2008). The Peleg model best described the sorption data of rice (Toğrul and Arslan, 2006) and tea (Arslan and Toğrul, 2006).

3.3. Specific surface area of sorption

The values of adsorption surface area of pepper corns were calculated using the *Mo* values obtained from the GAB equation. The values were 168.8, 125.6 and 123.2 m^2/g solids at 22, 30 and 37°C, respectively. The respective sorption area of the desorption are 164.9, 164.9 and 154.0 m^2/g solids. These values are within the range commonly obtained for food products (100-250 m^2/g solid) (Cassini et al., 2006). Water sorption can be influenced by surface area, composition, porosity and the number of binding sites. According to Swahney et al. (2013), temperature has significant influence on properties of bound water and surface area of adsorbent. Increase in temperature appears to reduce the sorption area of black pepper whole corns in both the sorption isotherms, however, the decrease is larger during adsorption compared to desorption.

3.4. Isosteric heat of sorption and sorption entropy

The a_w data generated using GAB model was used to calculate the isosteric heat of sorption and sorption entropy. The isosteric heat of sorption and sorption entropy of both adsorption and desorption isotherms as a function of EMC are shown in Fig. 5. The isosteric heat of sorption quantifies the interaction forces between the water vapour molecules and the surface of peppercorns. As seen in Fig. 5, the net isosteric heat of sorption is highly dependent on the EMC; with the

energy required for sorption increasing at low MC and after reaching a maximum value decreasing exponentially with increasing EMC. Similar trend has been observed in previous studies (Taitano et al., 2012; Toğrul and Arslan, 2007). This could be due to the different strength of water binding. Initial occupation of the highly active polar sites on the surface could be difficult due to high interaction energy and subsequent filling of the less active sites could become possible with low energy (Arslan and Toğrul, 2005; Moreira et al., 2008). The net isosteric heat decreased rapidly until around 10% EMC and after that it decreased at very slow rate with increasing EMC. The maximum isosteric heat for adsorption and desorption was 28.06 and 73.31 kJ/mol, respectively (Fig. 5) which was found at 4% EMC. This is closer to the obtained M_0. The isosteric heat of desorption was higher than that of adsorption at lower EMC however, the difference rapidly decreases at higher EMCs. In contrast to the crushed chillies (Arslan and Toğrul, 2005) marked difference in net isosteric heat of sorption was found between adsorption and desorption curves of black pepper whole corns. Similar trend has also been observed in yellow dent corn (Samapundo et al., 2007). The information on the magnitude of heat of sorption at a particular MC, could give an indication on the state of the absorbed water and could help to identify the physical, chemical and microbiological stability of food.

Similar to the net isosteric heat, the sorption entropy follows the same trend strongly depending on the EMC (Fig. 5). Yet again the entropy for desorption shows some differences to that for adsorption. Generally lower entropy was determined to occur during adsorption than during desorption. The maximum sorption entropy of black pepper was 80.8 and 118.5 J/mol/K for adsorption and desorption, respectively. At around 20% EMC (dwb) both sorption curves approached to a minimum entropy and further increase in EMC results in adsorption and desorption having similar levels of entropy. At higher EMC the active sites on the surface could be occupied by the water molecules hence had less capacity for sorption thus reducing the entropy. Similar trends in sorption entropy has been previously reported in potatoes (McMinn and Magee, 2003), dried casein (Sawhney, 2011), almonds (Taitano et al., 2012), whey protein concentrate from buffalo milk (Sawhney et al., 2013) and in sorghum (Bonner and Kenney, 2013). Moreover, the plot of enthalpy (ΔH) versus entropy (ΔS) shows a linear relationship for adsorption (R^2 0.9998) and for desorption (R^2 0.993), which indicates the existence of the enthalpy-entropy compensation. This compensation theory can be used to investigate the physical and chemical phenomena during the adsorption process (Moreira et al., 2008).

3.5. Gibbs free energy change

The variability of Gibbs free energy ($-\Delta G$) change with EMC is shown for the three temperatures during adsorption in Fig. 6. It is clear that the ($-\Delta G$) decreases exponentially with increasing EMC. High ΔG indicates that there is high freedom of water adsorption due to hydrophilic properties in a food material (Taitano et al., 2012). Moreover, the ($-\Delta G$) at a specific moisture content was lower the higher the incubation temperature. ($-\Delta G$) is related to the energy required in

making sorption sites available, hence it becomes smaller with increase in temperature or EMC. Rate of increase in Gibbs free energy of adsorbent at higher EMCs was very slow. Similar trends were also observed with desorption, however, in contrast to adsorption a sharp decrease in free energy change was observed during desorption from 4% (37422±1880 J/mol) to 5% (6147±895 J/mol) EMC increase. Variability in ΔG during the adsorption and desorption is shown in Fig. 7. Above 5% EMC the difference in free energy change was not significant between adsorption and desorption isotherm at any temperature (22°C, p=0.619; 30°C, p=0.284; 37°C, p=0.307). According to Taitano et al. (2012), the influence of MC on the (-ΔG) is more pronounced when the MC is less than the M_0.

4. Conclusions

The moisture adsorption and desorption isotherms of whole black peppercorns were successfully generated by standard static gravimetric method using different saturated salt solutions at three temperatures. The sorption isotherms resulted in a shape of type III according to BET classification. The EMC increased with decreasing temperature at constant a_w. The EMC for desorption was generally higher than the adsorption for a particular a_w indicating the occurrence of hysteresis. The GAB and Peleg were the best models to describe the sorption isotherms of black peppercorns over the range of temperature and a_w studied. The net isosteric heat of sorption and sorption entropy increased with increasing moisture content until the monolayer level and followed by an exponential drop beyond this point. The Gibbs free energy change was shown to exponentially decrease with increasing moisture content. These calculated thermodynamic properties could be useful in designing drying processes and storage parameters for whole black peppercorns to ensure the microbial as well as the chemical stability.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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Nomenclature

BET	Brunauer-Emmett-Teller
dwb	Dry weight basis
DLP	Double log polynomial
EMC	Equilibrium Moisture Content
GAB	Guggenheim -Anderson-de Boer
RMSE	Root Mean Square Error
RSS	Residual Sums of Squares
wwb	Wet weight basis
$EMC_{exp,i}$	i^{th} value of the experimentally measured EMC

$EMC_{pred,i}$	i^{th} value of the predicted EMC
M_0	Monolayer moisture content (% dwb)
R_{ave}	Average of the residuals
χ^2	Reduced chi square
ΔG	Gibbs free energy change (J/mol)
ΔH	Enthalpy (kJ/mol)
$\Delta Hvap$	Heat of vaporisation (kJ/mol/K)
ΔH_B	Binding Energy (J/mol)
P (%)	Mean relative percentage deviation modulus
q_{st}	Net isosteric heat of sorption or enthalpy of sorption (kJ/mol)
Q_{st}	Total heat of sorption
R	Universal gas constant (8.314 J/mol/K)
R^2	Coefficient of determination
S	Solid surface Area (m^2/g solids)
ΔS	Sorption entropy (J/mol/K)
T	Temperature in Kelvin

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Figures:

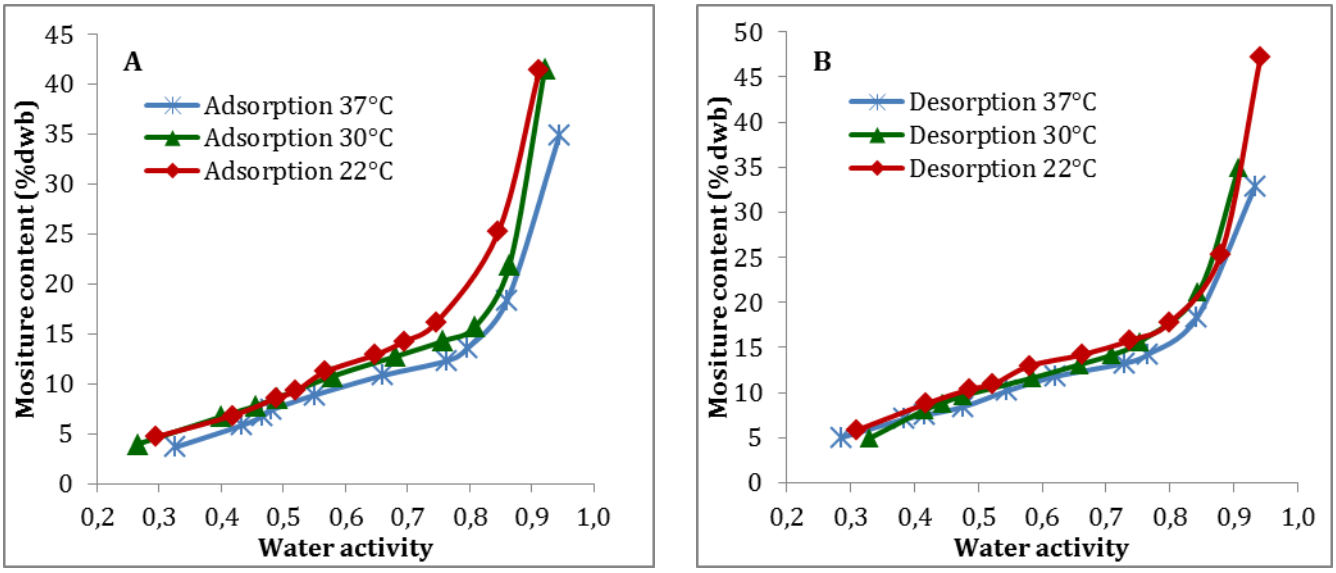


Fig. 1. Adsorption (A) and desorption (B) isotherms of whole black peppercorns at different temperatures.

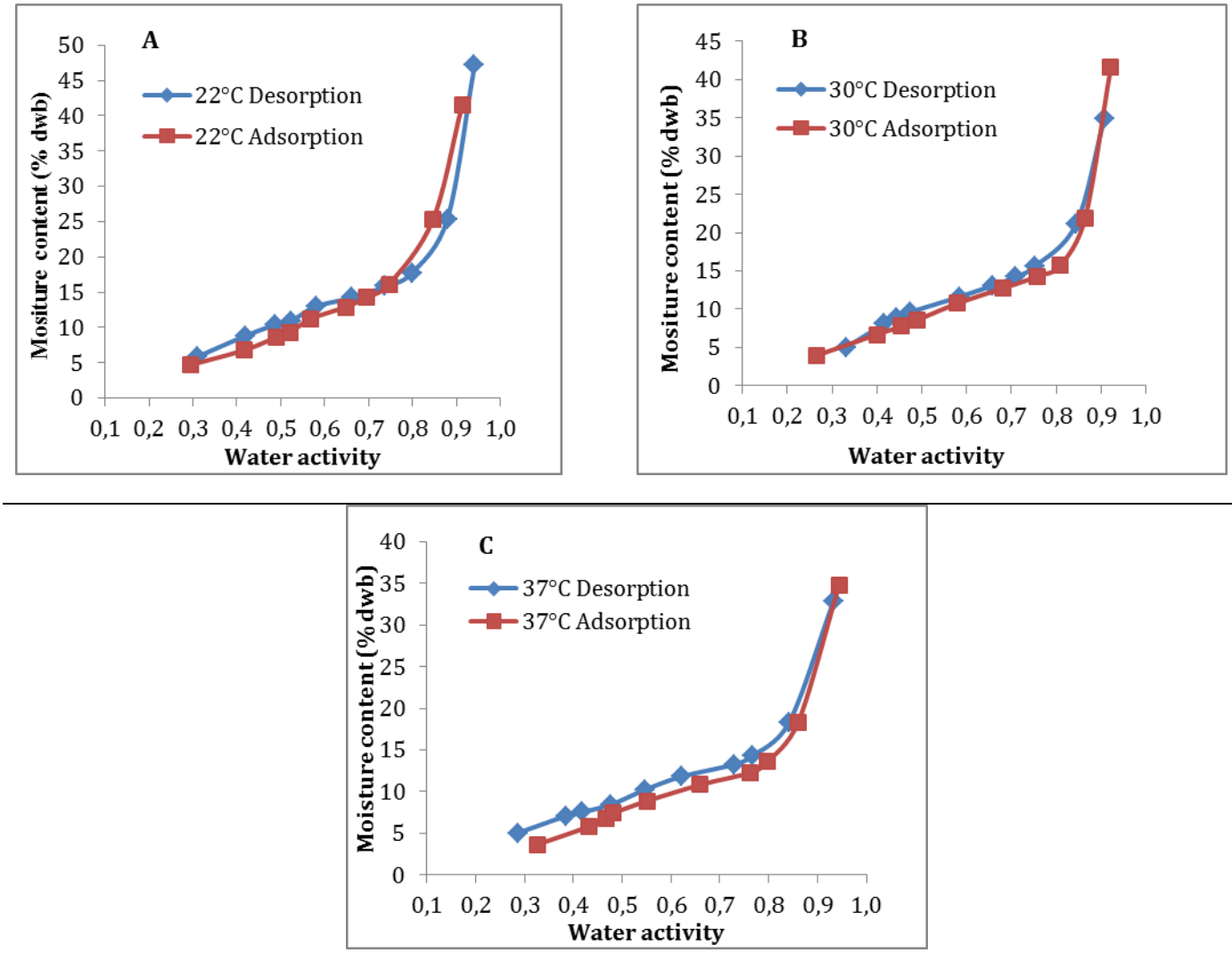


Fig. 2. Adsorption ( ) and desorption ( ) isotherms of whole black peppercorns at A) 22, B) 30 and C) 37°C showing the hysteresis.

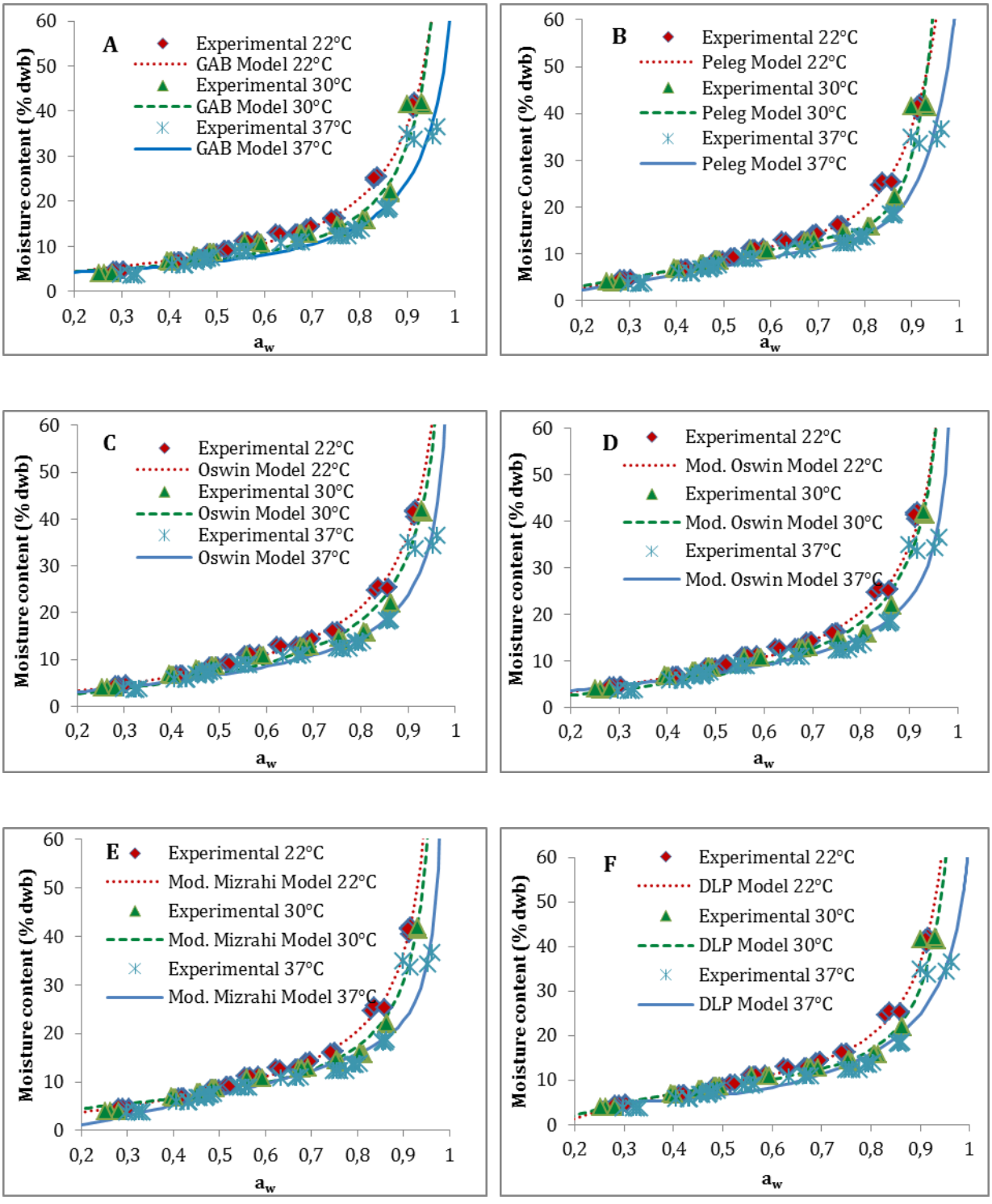
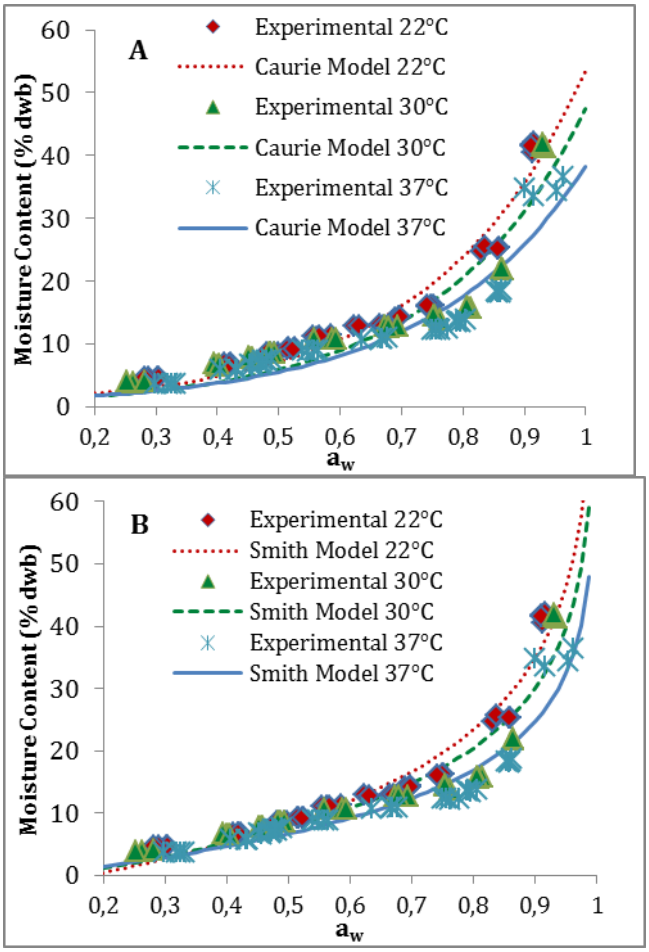


Fig. 3a. Mathematical models (best and moderate fitting A. GAB, B. Peleg, C. Oswin, D. modified Oswin, E. modified Mizrahi and F. double log polynomial (DLP)) fitted to the adsorption data of whole black peppercorns at different temperatures; experimental values are shown as markers (◆22°C,▲30°C and ✳37°C) and the model predictions are shown as lines (22°C, 30°C and — 37°C).


A
Experimental 22°C
Caurie Model 22°C
Experimental 30°C
Caurie Model 30°C
Experimental 37°C
Caurie Model 37°C
Moisture Content (% dwb)
60
50
40
30
20
10
0
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
a_w
B
Experimental 22°C
Smith Model 22°C
Experimental 30°C
Smith Model 30°C
Experimental 37°C
Smith Model 37°C
Moisture Content (% dwb)
a_w

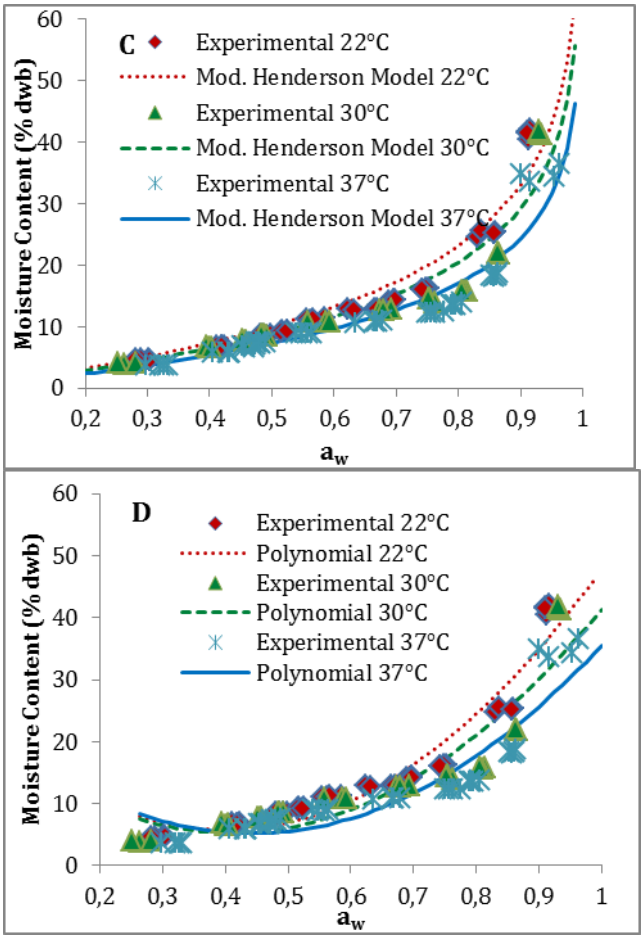


Fig. 3b. Mathematical models (poor fitting A. Caurie, B. Smith, C. modified Henderson and D. polynomial) fitted to the adsorption data of whole black peppercorns at different temperatures; experimental values are shown as markers (◆22°C,▲30°C,✳37°C) and the model predictions are shown as lines (..... 22°C, - - 30°C and ▬ 37°C).

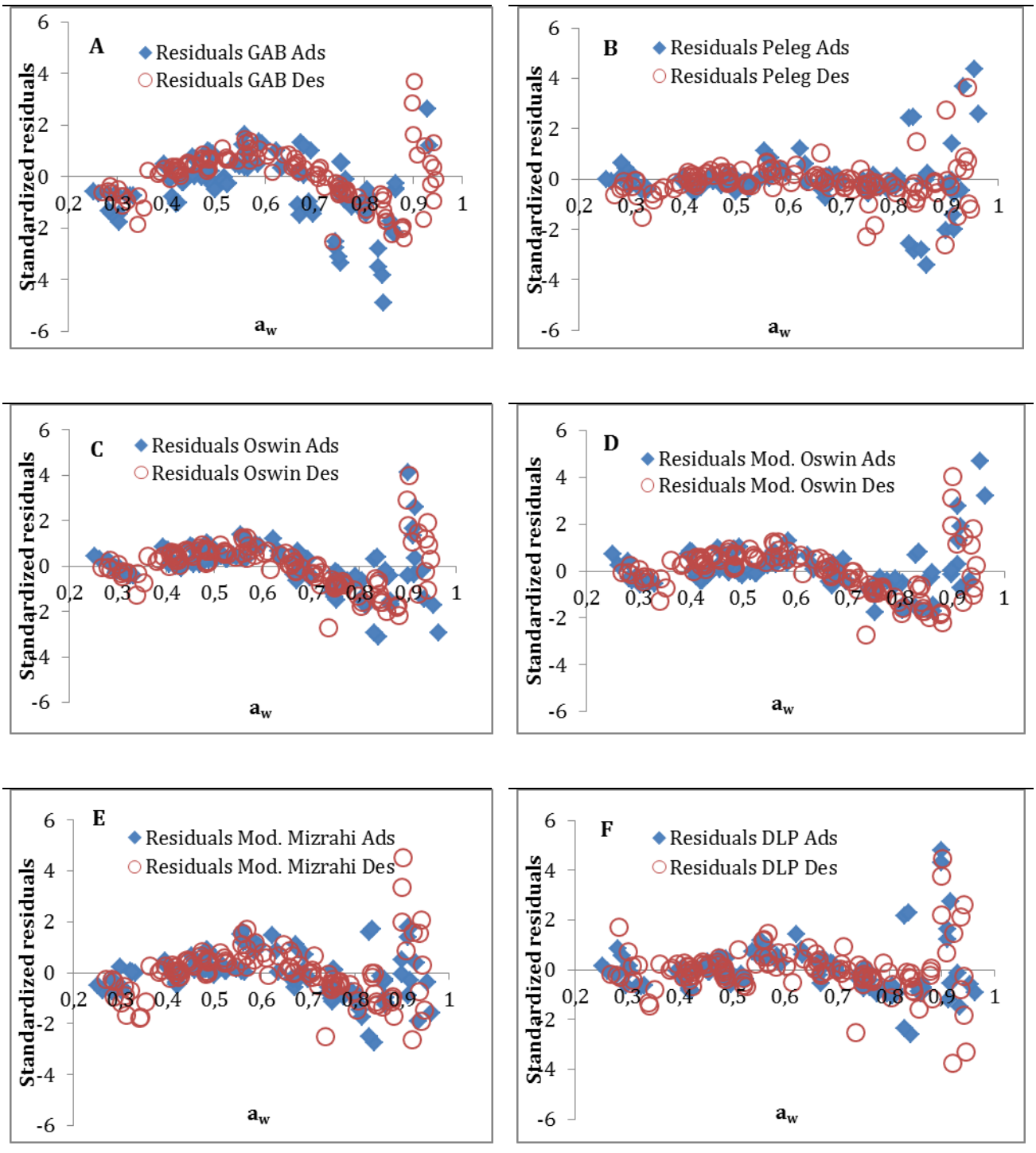


Fig. 4a. Residual plots (best and moderate fitting models A) GAB, B) Peleg, C) Oswin, D) modified Oswin, E) modified Mizrahi and F) double log polynomial (DLP)) of adsorption/Ads (◆) and desorption/Des (O) isotherms of whole black peppercorns fitted to different models.

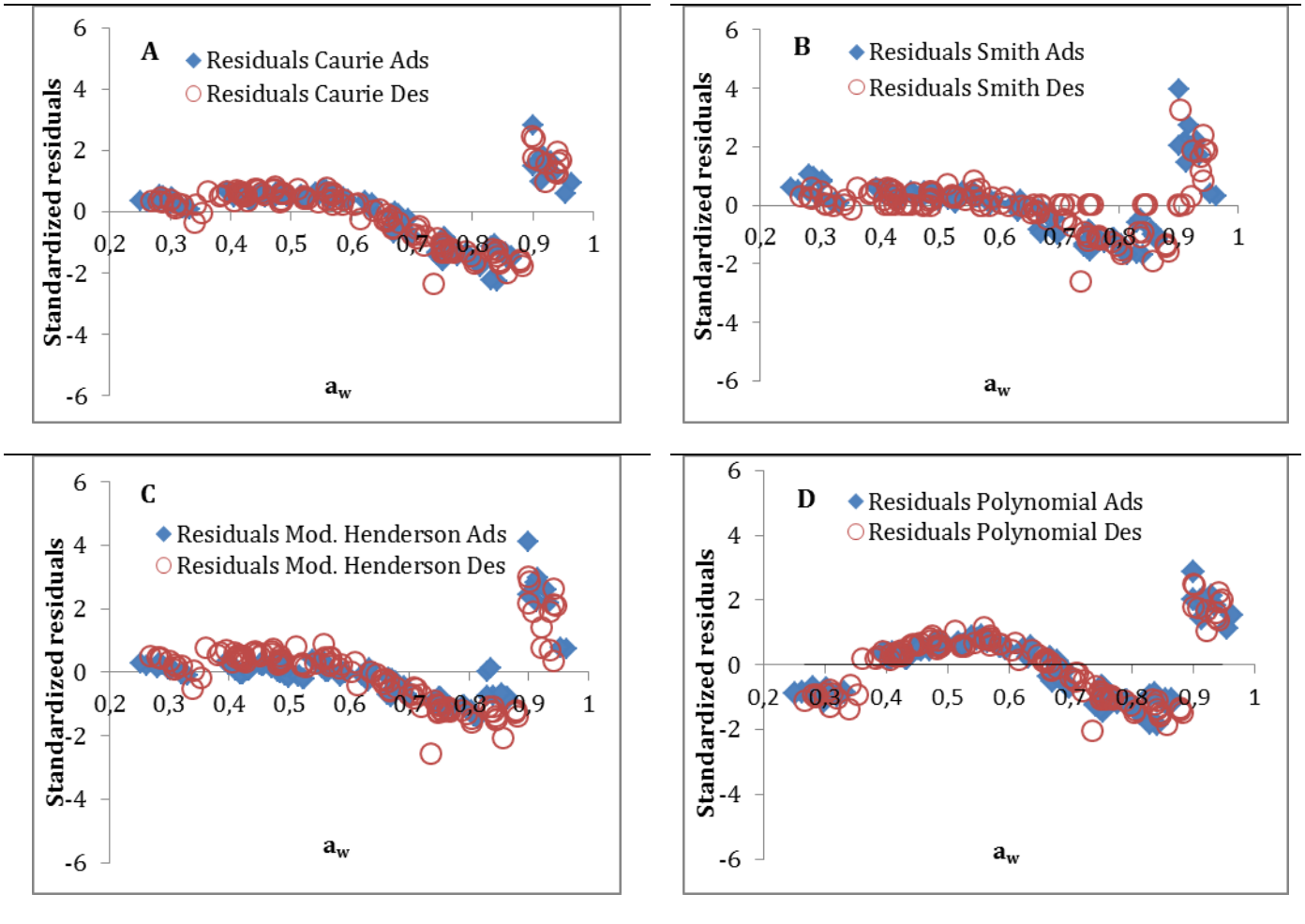


Fig. 4b. Residual plots (poor fitting models A) Caurie, B) Smith, C) modified Henderson and D) polynomial) of adsorption/Ads (◆) and desorption/Des (O) isotherms of whole black peppercorns fitted to different models

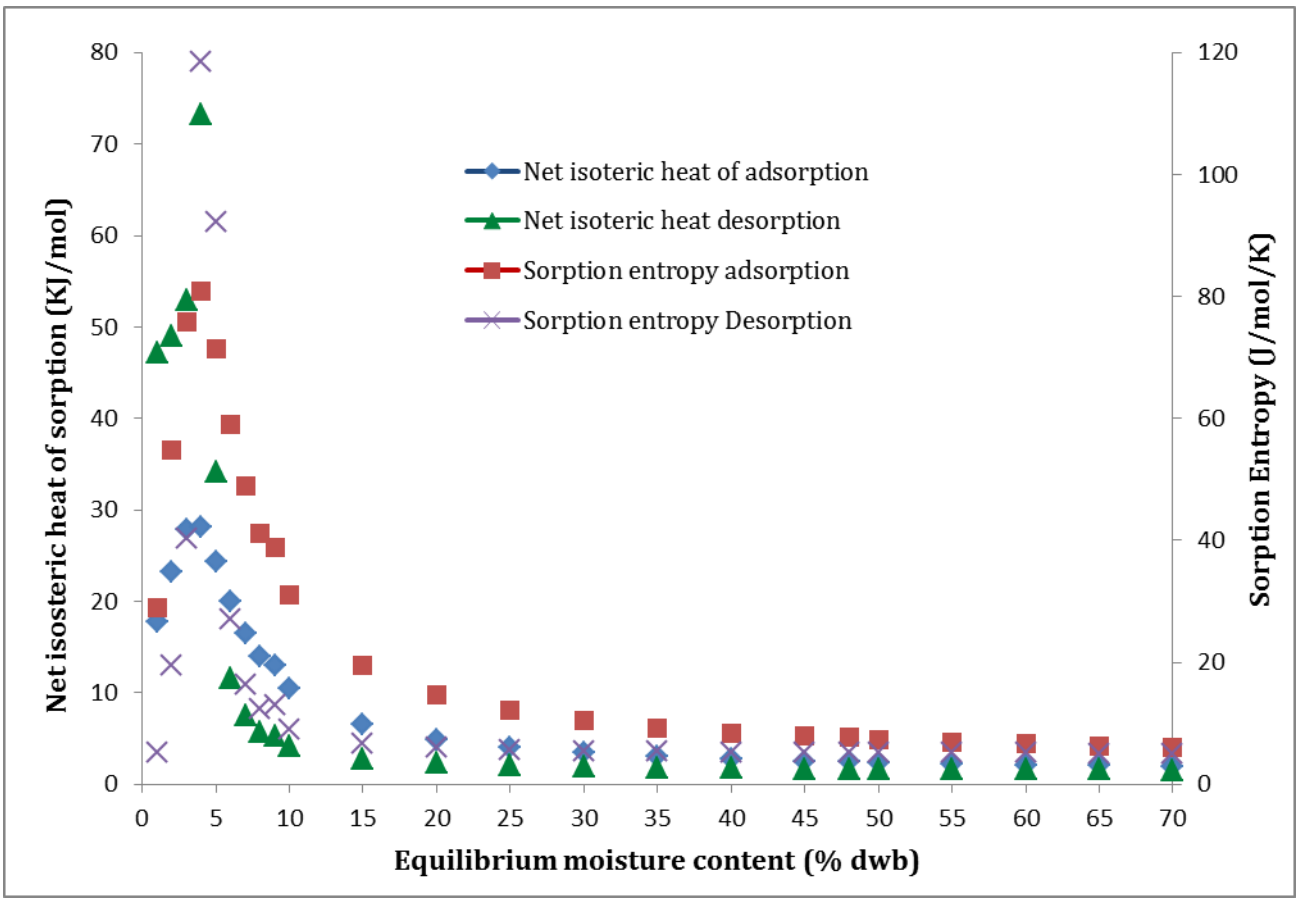


Fig. 5. Effect of moisture content on the net isosteric heat of sorption and sorption entropy of whole black peppercorns

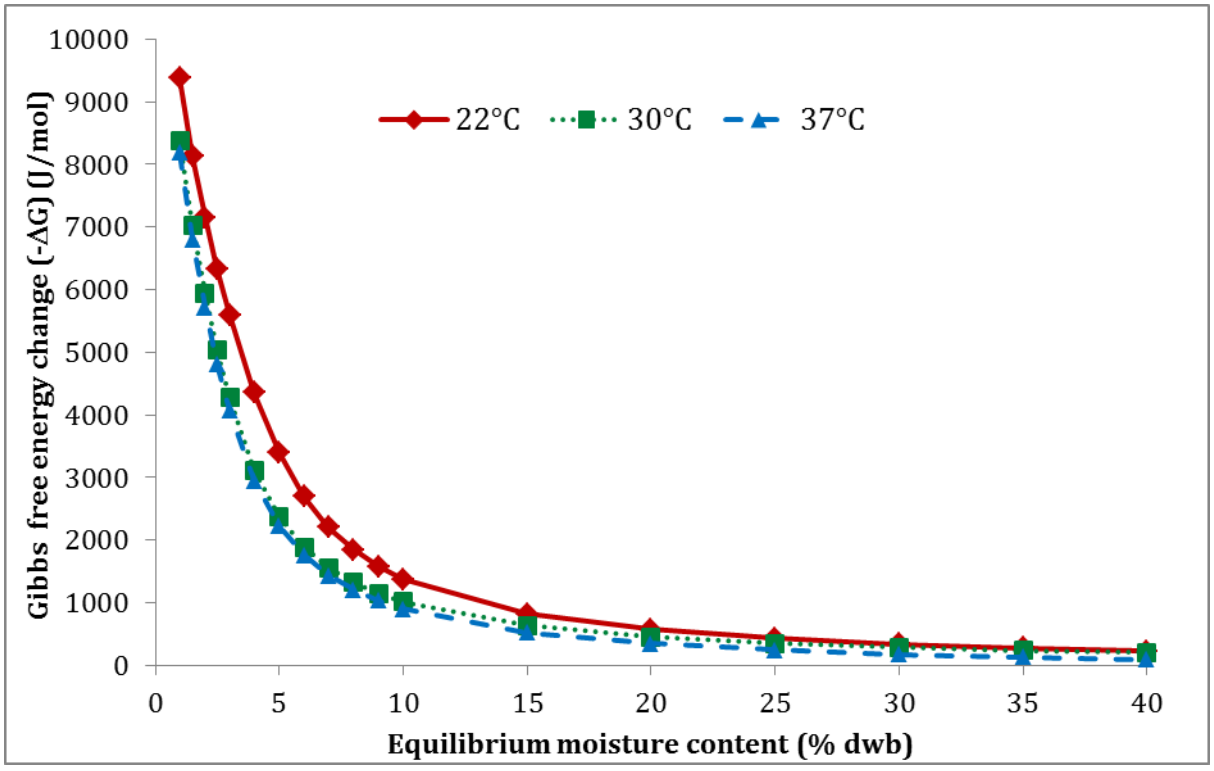


Fig. 6. Gibbs free energy change during adsorption of whole black peppercorns at different temperatures (22°C, 30°C and 37°C).

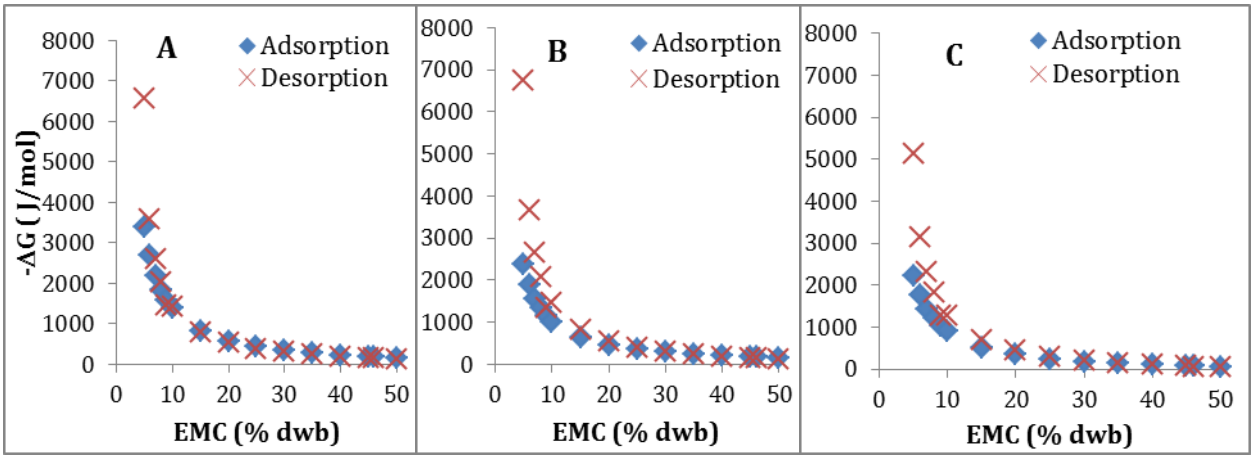


Fig. 7. Comparison of Gibbs free energy change during adsorption (◆) and desorption (X) of whole black peppercorns at different temperatures, A) 22°C, B) 30°C and 37°C.

Tables

Table 1. The models applied to describe the adsorption and desorption experimental data of whole black peppercorns

Model	Equation[a]	Parameters	Eq. No
BET (Brunauer. Emmett and Teller, 1938)	$MC = \frac{M_0 C a_w}{[(1-a_w)+(C-1)(1-a_w)a_w)]}$	M_0, C	1
GAB (Guggenheim -Anderson and de Boer, 1966)	$MC = \frac{M_0 C K a_w}{[(1-Ka_w)(1-Ka_w+CKa_w))]}$	M_0, C, K	2
	$C = C_0 \exp(\Delta H_C / RT)$		3
	$K = K_0 \exp(\Delta H_k / RT)$		4
Peleg (Peleg, 1993)	$MC = k_1 a_w^{n_1} + k_2 a_w^{n_2}$	k_1, k_2, n_1, n_2	5
Oswin (Oswin, 1946)	$MC = k(a_w/1-a_w)^n$	k, n	6
Modified Oswin (Chen, 2000)	$MC = (A-BT)\left(\frac{a_w}{1-a_w}\right)^C$	A, B, C	7
Modified Mirzahi (Mizrahi and Karel, 1977)	$MC = \frac{a + a_w(ca_w+b)}{(a_w-1)}$	a, b, c	8
Caurie (Caurie, 1970)	$MC = \exp(1+ba_w)$	a, b	9
Smith (Smith, 1947)	$MC = a - bIn\,(1-a_w)$	a, b	10
Modified Henderson (Henderson, 1952)	$MC = \{In(1-a_w)/[-k(T+c)]\}^{1/n}$	k, c, n	11
Polynomial (Samapundo et al., 2007)	$MC = a + ba_w + ca_w^2$	a, b, c	12
Double Log Polynomial (Bonner and Kenney, 2013)	$MC = b_3\,In(-ln(a_w))^3 + b_2\,In(-ln(a_w))^2 + b_1 ln(-lnK a_w) + b_0$	b_3, b_2, b_1, b_0	13

[a] Moisture Content is denoted by MC in all the equations

Table 2. Estimated parameters and performance criteria of the best and moderately fitting models applied to the experimental adsorption and desorption data of whole black peppercorns

Models and Parameters	Adsorption			Desorption		
GAB	**22°C**	**30°C**	**37°C**	**22°C**	**30°C**	**37°C**
M_0	4.78	3.56	3.49	4.67	4.67	4.36
C	11.9	12.1	12.7	9.07	4.65	6.61
K	0.97	0.99	0.95	0.95	0.95	0.93
R^2	1.00	0.97	0.99	0.97	0.97	0.96
R_{ave}	0.21	0.24	0.27	0.31	0.07	0.09
c^2	0.61	7.60	6.17	3.92	2.35	2.74
P (%)	5.47	11.0	10.3	11.68	10.24	9.52
RSS	22.4	83.8	36.2	144.9	87.0	101.5
RMSE	0.75	1.67	0.95	1.90	1.48	1.59
PELEG						
k_1	80.8	168.4	51.5	92.5	66.5	41.7
k_2	22.3	19.4	17.3	21.5	19.9	15.8
n_1	14.5	23.7	17.6	20.5	14.6	11.7
n_2	1.31	1.15	1.24	1.03	1.05	0.83
R^2	1.00	1.00	1.00	1.00	0.98	0.97
R_{ave}	-0.01	-0.20	0.22	-0.01	-0.01	-0.01
c^2	0.59	9.59	7.06	0.43	1.50	2.08
P (%)	3.42	4.67	6.78	2.99	6.04	6.09
RSS	21.1	249.2	254.2	15.4	54.0	74.7
RMSE	0.73	2.88	2.52	0.62	1.16	1.37
OSWIN						
K	8.36	6.97	6.74	9.19	8.91	8.39
n	0.67	0.70	0.58	0.57	0.57	0.52
R^2	1.00	0.96	0.99	0.97	0.97	0.96
R_{ave}	0.05	-0.12	0.26	0.20	0.07	0.05
c^2	1.03	4.62	7.10	1.89	2.39	2.79
P (%)	4.89	15.3	10.6	10.3	9.46	7.92
RSS	39.0	129.3	269.7	135.3	90.9	106
RMSE	0.99	2.08	2.60	1.84	1.51	1.63
Modified OSWIN						
A	33662.8	204907.6	182019.9	-33660.3	-148653.2	256922.5
B	-1529.8	-6830.0	-4919.3	1530.4	4955.4	6944.1
C	0.65	0.70	0.52	0.57	0.57	0.52
R^2	1.00	0.96	0.92	0.97	0.97	0.96
R_{ave}	0.53	-0.10	-0.07	0.17	0.08	0.05
c^2	1.87	4.76	6.54	3.66	2.46	2.87
P (%)	4.96	15.4	10.3	10.3	9.55	7.92
RSS	69.3	128.4	241.9	135.4	90.9	106

RMSE	1.32	2.07	2.46	1.84	1.51	1.63
Modified MIZRAHI						
a	-1.12	-2.84	2.88	-4.06	-2.46	-2.02
b	-11.0	-5.02	-22.3	-5.71	-8.71	-9.84
c	9.12	5.30	18.5	7.58	8.81	10.3
R^2	0.99	0.95	0.90	0.99	0.97	0.96
R_{ave}	0.00	-0.37	0.00	-0.01	0.00	0.00
c^2	0.67	1.87	7.66	1.36	2.02	2.85
P (%)	4.28	9.38	8.09	7.20	8.23	6.55
RSS	24.9	50.6	283.4	50.1	74.6	105.5
RMSE	0.79	1.30	2.67	1.12	1.37	1.62
Double Log Polynomial (DLP)						
b_0	6.25	6.42	5.35	7.66	6.66	6.78
b_1	-8.48	-7.13	-2.15	-10.8	-10.5	-5.52
b_2	-2.98	-3.60	3.94	-6.81	-6.11	-0.73
b_3	-2.32	-2.33	0.46	-2.83	-2.83	-0.89
R^2	1.00	0.95	0.93	1.00	0.98	0.96
R_{ave}	0.01	0.00	0.00	0.00	0.00	0.00
c^2	0.62	5.71	5.87	0.56	1.61	2.64
P (%)	4.22	6.19	13.9	3.68	4.55	6.17
RSS	22.3	148.5	211.2	20.1	58.0	95.0
RMSE	0.75	2.23	2.30	0.71	1.20	1.54

Table 3. Estimated parameters and fitting criteria of the models (poor fitting) applied to the experimental adsorption and desorption data of whole black peppercorns.

Models and Parameters	Adsorption			Desorption		
CAURIE	**22°C**	**30°C**	**37°C**	**22°C**	**30°C**	**37°C**
a	-0.04	-0.30	-0.22	0.19	0.51	0.49
b	4.01	4.16	3.87	3.71	3.21	3.08
R^2	0.95	0.85	0.88	0.87	0.91	0.88
R_{ave}	0.34	0.51	0.53	0.56	0.22	0.28
c^2	6.02	14.75	9.22	18.2	6.47	7.39
P%	17.00	27.7	22.8	23.5	15.3	18.7
RSS	228.8	413.0	350.5	692.9	245.7	281
RMSE	2.39	3.71	2.96	4.16	2.48	2.65
SMITH						
a	-3.18	-1.88	-1.01	-0.94	-0.04	0.93
b	16.5	13.9	11.2	14.7	13.0	10.8
R^2	0.95	0.87	0.91	0.91	0.93	0.92
R_{ave}	0.00	-0.17	0.00	0.00	0.00	0.00
c^2	5.55	11.4	6.87	11.5	4.62	4.67
P%	14.3	19.8	13.5	15.9	11.9	11.7
RSS	211.0	319.8	261.2	437.6	176	178
RMSE	2.30	3.27	2.56	3.31	2.10	2.11
Modified Henderson						
K	0.04	0.08	0.06	0.19	0.14	0.15
c	-19.6	-27.9	-33.6	-18.6	-25.8	-31.9
n	0.70	0.48	0.49	0.11	0.13	0.12
R^2	0.93	0.86	0.91	0.91	0.93	0.92
R_{ave}	-0.87	-0.68	-0.34	-0.30	-0.01	0.29
c^2	8.29	12.8	7.37	12.1	4.75	5.06
P%	13.8	12.3	11.0	13.2	11.8	15.8
RSS	306.8	345.8	272.6	447.2	175.6	187.2
RMSE	2.77	3.40	2.61	3.34	2.10	2.16
Polynomial						
a	24.21	22.42	24.33	31.24	23.35	19.18
b	-92.5	-84.0	-86.5	-108.3	-78.2	-63.5
c	116.0	102.9	97.7	123.4	94.8	79.2
R^2	0.93	0.82	0.86	0.85	0.90	0.88
R_{ave}	0.00	-0.11	0.00	0.00	0.00	0.00

c^2	8.38	19.09	11.0	20.7	6.91	7.72
P%	19.5	29.8	26.9	24.7	18.3	19.7
RSS	310.2	515.4	405.9	766.9	255.6	285.5
RMSE	2.78	4.14	3.19	4.38	2.53	2.67